Sains Malaysiana 43(1)(2014): 95–101

A Novel Ruthenium-tungsten Bimetallic Complex Dye-Sensitizer for Photoelectrochemical Cells Application

(Kompleks Baru Dwilogam Rutenium-tungsten Sebagai Bahan Pewarna Pemeka untuk Aplikasi Sel Fotoelektrokimia)

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ABSTRACT

A novel bimetallic double thiocyanate-bridged ruthenium and tungsten metal complex containing bipyridyl and dithiolene co-ligands was synthesized and the behavior of the complex as a dye-sensitizer for a photoelectrochemical (PEC) cell for a direct water splitting reaction was investigated. The ligands and metal complexes were characterized on the basis of elemental analysis as well as UV-Vis, Fourier transform infrared (FTIR) and nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectroscopy. Cyclic voltammetry of the bimetallic complex showed multiple redox couples, in which half potentials $E_{1/2}$ at 0.625, 0.05 and 0.61V were assigned as the formal redox processes of Ru(III)/Ru(II) reduction, W(IV)/W(V) and W(V)/W(VI) oxidations, respectively. Photocurrent measurements were performed in homogeneous system and TiO_2 was used as the photoanode for photocurrent measurements. Current density generated by the bimetallic complex was higher than that of N3 commercial dye which suggested that the bimetallic complex donated more electrons to the semiconductor.

Keywords: Bimetallic; bipyridyl; dithiolene; dye-sensitizer

ABSTRAK

Kompleks dwilogam baru dengan ligan jejambat tiosianat berasaskan logam rutenium dan tungsten yang mengandungi ko-ligan bipiridil dan ditiolena telah berjaya disintesis. Keupayaannya sebagai bahan pewarna pemeka untuk kegunaan sel fotoelektrokimia (PEC) bagi pembelahan molekul air secara terus juga telah dikaji. Ligan dan kompleks logam telah dicirikan berdasarkan kaedah analisis mikro unsur CHNS; spektroskopi infra-merah, ultralembayung-cahaya nampak, ^{1}H dan ^{13}C NMR. Analisis voltammetri berkitar menunjukkan kompleks dwilogam mempunyai beberapa puncak redoks, antaranya adalah puncak redoks pada potensi separuh $E_{1/2}$ -0.625, 0.05 dan 0.61V yang merupakan keupayaan formal redoks bagi proses penurunan Ru(III)/Ru(II) dan pengoksidaan W(IV)/W(V) dan W(V)/W(VI). Pengukuran fotoarus dilakukan dalam sistem homogen dan TiO_2 digunakan sebagai fotoanod. Ketumpatan arus yang dihasilkan oleh kompleks dwilogam lebih tinggi berbanding yang dihasilkan oleh bahan pemeka komersil N3 yang bermakna elektron yang didermakan kompleks dwilogam lebih besar berbanding yang didermakan oleh molekul N3.

Kata kunci: Bahan pewarna pemeka; bipiridina; ditiolena; dwilogam

INTRODUCTION

Photosynthesis is a natural process of energy transformation that occurs in plants, algae and bacteria using sunlight. Light energy absorbed by chlorophyll is used to split water molecules into O_2 and H^+. The H^+ binds with CO_2 from the atmosphere to form glucose, an energy-rich sugar. Artificial photosynthesis technology mimics the processes of natural photosynthesis to produce hydrogen, which is used in fuel cell technology to generate energy in the form of electricity (Allakhverdiev et al. 2010; Joya & de Groot 2012; Young et al. 2012). Artificial photosynthesis systems use transition metal complexes to harness light, catalyze the reaction and act as the reaction center (Najafpour & Allakhverdiev 2012).

Dye-sensitized photoelectrochemical (PEC) cells are a type of artificial photosynthesis system that uses a transition metal complex as the photosensitizer to enhance the sensitivity of the photoelectrode semiconductor to sunlight, which enables a wider range of radiation wavelengths to be absorbed (Abe et al. 2000; Minggu et al. 2010). Ruthenium bipyridyl complexes are the transition metal complexes that are most often used as the sensitizer in solar cells (Grätzel 2003). Currently, research on dye-sensitizers is focused on increasing the efficiency of light absorption (i.e. molar extinction coefficient) and to find alternative dyes with enhanced properties and capabilities (Aiga & Tada 2005; Nazeeruddin et al. 2005; Vougioukalakis et al. 2011). Improvement upon the performance of monometallic complex sensitizers is challenging because the number of possible electron transfers is limited. One way to improve the efficiency of dye-sensitized PEC cells is to use a bimetallic complex as a sensitizer (Argazzi et al. 2001; Kleverlaan et al. 2000; Zhao et al. 2012).

Various bimetallic complexes with combinations of metals, ligands and bridging ligands have been synthesized and used as dye-sensitizers (Arifin et al. 2012a). However, difficulties in the preparation of bimetallic complexes that allow electrons to transfer from one metal center to the other have caused bimetallic complexes to be less efficient than monometallic complexes. One of the major challenges is to facilitate electron transfer, which requires the bridging ligands of bimetallic complexes to be conjugated. Most of the bimetallic complexes that have been reported have large non-rigid bridging ligands, which enable charge recombination to occur because a long duration required for electron and energy transfers to occur from one metal center to the other (Balzani et al. 1996; Chiorboli et al. 1999). In most cases adsorption of the complexes occurs only on the outer surface of the photoelectrodes, which contributes to low efficiencies. Furthermore, most of the simple bridging ligands are non-rigid, which allows sterics to affect the geometry and causes the determination of the electrochemical properties to be difficult (Hofmeiera & Schubert 2004). An ideal bimetallic complex used as the dye-sensitizer in a PEC solar cell application should have a simple and rigid bridging ligand(s) that satisfies the requirements for efficient intramolecular energy transfer. Bimetallic complexes are still being designed and synthesized to satisfy these conditions to improve the efficiency of solar cells.

In this paper we describe the synthesis of a novel bimetallic complex that was designed to have a rigid but efficient intramolecular energy transfer pathway to satisfy the requirement of dye-sensitizer for PEC applications. The preparation, characterization, electrochemical and PEC analyses of the novel thiocyanate-bridged bimetallic complex, which was based on ruthenium and tungsten metals with bipyridyl and dithiolene co-ligands, are presented. The model complex reported in this paper is a ruthenium-(4,4'dimethyl-2,2′-bipyridine)-isothiocyanato-tungsten[bis-(phenyl-1,2-ethilenodithiolenic)], which is abbreviated as BM. Bipyridyl ligands such as 4,4'dimethyl-2,2′-bipyride has been widely used in dye-sensitizers (Balzani & Juris 2001; Chakraborty et al. 1999), while, dithiolene ligands are electron rich and redox non-innocent (i.e. they exhibit a variety of redox states with unique optical properties) (Goddard & Holm 1999; Ward & McCleverty 2002). There are relatively few reports that used bimetallic complexes with thiocyanate as the bridging ligand (Banerjee et al. 2005; Navarro et al. 1997). Thiocyanate, an ambidentate ligand that attaches to a metal center in either an end-on (1,1-μ-SCN, 1,1-μ-NCS) or end-to-end (1,3-μ-SCN) configurations, has been reported to be used as a bridging ligand to link ruthenium and tungsten (Shen & Feng 2002).

Experimental Details

Dichloro(*p*-cymene)ruthenium(II) dimer, 4,4'-dimethyl-2,2'-bipyridine, tungsten hexacarbonyl, ammonium thiocyanate (NH_4NCS), benzoin, phosphorus pentasulfide and solvents were purchased from Sigma–Aldrich and used as received. IR spectra were acquired using a Thermo Nicolet 6700 FTIR spectrometer. The ^{1}H and ^{13}C NMR spectra were acquired on an Avance Bruker 400 MHz spectrometer. Electronic absorption spectra were acquired on a Varian Cary 5000 UV–Vis spectrophotometer. Elemental analyses were performed using an Elemental Micro Cube CHNS analyzer. Electrochemical and PEC analyses were performed using a Princeton Applied Research (PAR) Ametek Versastat 4 potentiostat.

Ruthenium-[bis(4,4'-dimethyl-2,2′-bipyridyl)-isothiocyanato] was synthesized by mixture of 4,4'-dimethyl-2,2'-bipyridine (0.1 g, 0.34 mmol) and dichloro(*p*-cymene)ruthenium(II) dimer (0.05 g, 0.081 mmol) in dry, argon-degassed dimethyl formamide (DMF) (25 mL). The mixture was then heated to 150°C for 4 h. $NH_4NCS_{(s)}$ (0.39 g, 5.1 mmol) was added to the dark green solution and the mixture was heated at 150°C for an additional 4 h. After evaporation of the DMF, a purple residue was suspended in water (150 mL). The mixture was then extracted with diethylether (Et_2O) and washed with distilled water producing a purple solution. The Et_2O was removed by evaporation resulting in a dark purple solid with a 39% yield. IR spectrum (cm^{-1}): 3459 (N-H); 2931(C-H); 2105 & 1984 (NCS); 1678 (C=C aromatic), 1389 & 1459 (CH_3). UV/Vis spectrum l_{max}/nm ($\varepsilon \times 10^4$ M^{-1} cm^{-1}) in CH_3CN solution: 345 nm (20800); 395 nm (7100) & 550 nm (7200). Elemental CHNS analysis, % (required): C 52.10 (52.32); H 4.65 (4.13); N 15.93 (15.95) & S 8.94 (10.91).

The dithiolene carbonyl complex of tungsten $[W(S_2C_2Ph_2)_2(CO)_2]$ was synthesized via two step reactions, i.e. synthesis of tioester-1,2-dithiol $[Ph_2C_2S_2P(O/S)(O)_{1/2}]_2$ and synthesis of dithiolene carbonyl complex. The tioester was synthesized by dissolve benzoin (30 g) and phosphorus pentasulfide (45 g) in dry dioxane (250 mL). The mixture was refluxed for 3-4 h in an N_2 atmosphere. Hydrogen sulfide produced from the reaction was trapped using lead acetate. The mixture was cooled to room temperature and then filtered. The filtrate was concentrated *in vacuo*, which resulted in a dark red oil with a 37.5% yield. IR spectrum (cm^{-1}): 1254 (P=O); 1081; 958 (P-O & P-O-P) & 870 (P=S). UV/Vis spectrum l_{max}/nm ($\varepsilon \times 10^4$ M^{-1} cm^{-1}) in acetone solution: 300 nm (35000) & 400 nm (23000). Elemental CHNS analysis, % (required): C 55.67 (55.07); H 3.73 (3.30) & S 24.60 (25.91).

A solution of tungsten hexacarbonyl ($W(CO)_6$) (1 g) in tetrahydrofuran (THF) (40 mL) was irradiated with UV light under an N_2 atmosphere at room temperature for 2 h to generate the $W(CO)_5$THF intermediate. The thioester (0.5 g) was added to the solution and the mixture was stirred for approximately 1 h at room temperature. The solvent was removed under reduced pressure. An orange-red solid was isolated with a 39% yield upon the addition of 30 mL of an Et_2O/hexane mixture (1:2 v:v) at approximately -15°C. IR spectrum (cm^{-1}): 3026 (C-H); 2071 & 1980 (C=O); 1677 cm^{-1} (C=C); 1155 cm^{-1} & 697 (C-S). Elemental CHNS

Analysis, % (required): C 55.28 (55.07); H 3.00 (2.78) & S 15.56 (17.70).

Although the general preparation of BM was reported earlier (Arifin et al. 2011), a detailed synthetic method for producing BM is described here. A solution of ruthenium-[bis(4,4'-dimethyl-2,2′-bipyridyl)-isothiocyanato] (0.06 g) in CH_3CN (5 mL) was added to a solution of tungsten ($W(S_2C_2Ph_2)_2(CO)_2$) (0.06 g) in CH_3CN (5 mL) and then the mixture was stirred at room temperature for 3 h. A black-brown solid and cloudy-white solution formed after cold water (20 mL) was added. The supernatant liquid was decanted and the solid was filtered, which resulted in a black-brown solid with a 10% yield. ^{1}H NMR (600 MHz, DMSO) d (ppm): 7.93-9.26 (12H of bipyridyl); 6.92-7.88 (20H of benzene) & 2.49 (CH_3). ^{13}C NMR (600 MHz, DMSO) d (ppm): 39.91 (CH_3); 55.61 (NCS); 114.48 (C=C); 126.76 & 137.37 (benzene); 151.65; 157.01 & 157.89 (bipyridyl). IR spectrum (cm^{-1}): 3418 (N-H); 2933 (C-H); 2095 & 1980 (1,3-μ-SCN); 1616 (C=C); 1450 & 1493 (CH_3) & 698 (C-S). UV/Vis spectrum l_{max}/nm ($\varepsilon \times 10^4$ M^{-1} cm^{-1}) in DMF solution: 330 (29800); 375 (14600), 535 (12500) & 712 (890). Elemental CHNS Analysis (%): C 51.02 (52.37); H 3.96 (3.92); N 6.69 (6.54) & S 16.56 (17.70).

The electrochemical properties of the complex were investigated using cyclic voltammetry using a platinum disk as the working electrode, a platinum wire as an auxiliary electrode and an Ag/AgCl as the reference electrode. The redox potentials of the complex (0.1 mM) were measured in a solution of DMF that contain 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) electrolyte in a nitrogen atmosphere at room temperature. A similar set up was used for the PEC analysis, except the TiO_2 thin film was used as the working electrode. The preparation, characterization and properties of TiO_2 electrodes were reported in our earlier communication (Arifin et al. 2012b). The PEC investigation was performed in a deaerated solution of water:DMF (4:1) that contained the complex (5×10^{-5} M) as the sensitizer. The solution was deoxygenated with nitrogen gas for 5 min. The current density on the surface of the TiO_2 electrodes was measured in the dark and under illumination using a 400 watt xenon lamp.

Results and Discussion

The synthesis route of BM, which was formed by the condensation reaction of ruthenium-[bis(4,4'-dimethyl-2,2′-bipyridyl)-isothiocyanato] (abbreviated [$Ru(dmtbpy)_2NCS_2$]) and [$W(S_2C_2Ph_2)_2(CO)_2$] complexes. The starting ruthenium bipyridyl complex [$Ru(dmtbpy)_2NCS_2$] was prepared from the reaction of 4,4'-dimetyl-2,2'-bipyridine with dichloro(*p*-cymene) ruthenium(II) dimer and NH_4NCS. The synthetic method was based on the synthesis of ruthenium complexes reported by Klein et al. (2005). The infrared spectrum of [$Ru(dmtbpy)_2NCS_2$] (KBr pellet) exhibited bands attributed to the following functional groups: A tertiary amide (N-H) at 3459 cm^{-1}, a n(C-H) aromatic at 2937 cm^{-1}, a thiocyanate band with a shoulder at 2105 cm^{-1}, a n(C=C) for aromatic at 1678 cm^{-1} and a -CH_3 stretching at 1389 cm^{-1}. A weak band observed at 1984 cm^{-1} was due to both the aromatic and methyl groups (Coates 2000). The UV-Vis spectra of the [$Ru(dmtbpy)_2NCS_2$] and the N3 commercial dye in DMF were similar, which showed three absorption bands at 345 nm (e = 20800 $M^{-1}cm^{-1}$), 395 nm (e = 7100 $M^{-1}cm^{-1}$) and 550 nm (e = 7200 $M^{-1}cm^{-1}$) assigned to metal to ligand charge transfer (MLCT) band. The CHNS elemental analysis was consistent with the expected compound with an empirical formula of $C_{26}H_{20}N_6S_2Ru$ for [$Ru(dmtbpy)_2(NCS)_2$] complex.

The $W(S_2C_2Ph_2)_2(CO)_2$ complex was first reported by Schrauzer et al. (1965) and has been further studied by many other researchers. The preparation of ($W(S_2C_2Ph_2)_2(CO)_2$) is accomplished via the reaction of the photogenerated intermediate, $W(CO)_5THF$, with a thioester prepared from benzoin and P_4S_{10}. The ($W(S_2C_2Ph_2)_2(CO)_2$) complex is a purple-red solid, which was soluble in CH_3CN, THF and dichloromethane, but insoluble in non-polar solvents. The physical characteristics of the ($W(S_2C_2Ph_2)_2(CO)_2$) prepared in this report were similar to previous report (Chandrasekaran et al. 2009). Notably, the complex was stable in a solid phase below 4°C (refrigeration) but was unstable in solution form. The nCO signals in the ($W(S_2C_2Ph_2)_2(CO)_2$) complex was observed at 2071 (w) and 1980 cm^{-1} (s) which are comparable to the previously reported bis(dithiolene) complexes (Asali & Janaydeh 2003). The infrared spectrum also shows other characteristic bands at 2953 cm^{-1} (C-H aromatic), 1677 cm^{-1} (C=C aromatic) and 1155 cm^{-1} (C-S).

The condensation of ($Ru(dmtbpy)_2(NCS)_2$) and ($W(S_2C_2Ph_2)_2(CO)_2$) was performed in DMF at room temperature to give BM molecule as a dark brown solid after 8 h. Decantation of the liquid was an important step in the procedure to avoid loss of the product before filtering. An infrared spectroscopy is very useful to identify the formation of the bimetallic complex quickly through the observation of a band at 2115 cm^{-1} for NCS group. The NCS frequency shifted to a slightly higher value than that of complex (**I**), which indicates that the thiocyanate acts as a a bridging ligand. The UV/Vis spectrum in DMF showed absorption maxima at 330 nm (e = 29800 $M^{-1}cm^{-1}$), 375 nm (e = 14600 $M^{-1}cm^{-1}$), 535 nm (e = 12500 $M^{-1}cm^{-1}$), which were assign to MLCT bands and the 712 nm (e = 890 $M^{-1}cm^{-1}$) band was assigned to the *d-d* transition of the metal centres.

The ^{1}H and ^{13}C NMR spectra of the bimetallic complexes were observed as groups of multiple signals making an accurate assignment of chemical shifts for the methyl, benzene and bipyridyl moieties to be difficult. In the ^{1}H NMR spectrum, the methyl protons was observed at approximately 2.49 ppm and the signal has a total integration value of 12. The benzene protons were observed in multiple groups over the range of 6.92-7.88 ppm (20H), whereas the bipyridyl protons were observed at higher chemical shift as multiple groups over the range

of 7.93-9.26 ppm (12H). The ^{1}H NMR spectra indicates that the BM molecule was asymmetric. The ^{13}C signals were slightly much easier to interpret, with the chemical shift of the methyl groups appears at 39.91 ppm. The thiocyanate carbon was observed as a singlet at 55.61 ppm. Other peaks included an ethylene carbon at 114.48 ppm; signals for aromatic carbons from the dithiolene group at 126.76 and 137.37 ppm and three signals for the bipyridyl moieties at 151.65, 157.01 and 157.89 ppm. No peaks were observed with chemical shifts above 160 ppm indicating all the carbonyl ligands of the tungsten monometallic complex were removed. The signal for the carbonyl carbon in a similar molecule [$W(CO)_4$(ligand)(ligand)] was approximately 200 ppm (Pathania et al. 2007).

The elemental analysis result gives 51.25 (52.37), 3.96 (3.92), 6.69 (6.54) and 16.56 (17.70) for C, H, N and S, respectively, with theoretical values in parentheses. BM was soluble in polar aprotic solvents (e.g. DMF and DMSO) but was not soluble in THF, dichloromethane and non-polar solvents which makes drying the complex as a difficult task.

The electrochemical properties of complex BM were investigated by cyclic voltammetry in a 3-electrode cell with a platinum disk working electrode, Ag/AgCl reference electrode and a platinum wire counter electrode in DMF containing 1×10^{-4} M $TBAPF_6$ as the supporting electrolyte. The voltammograms of BM and the corresponding monometallic complexes are shown in Figure 1. Bimetallic BM complex exhibited multiple redox processes corresponding to one reversible redox couple, three quasi-reversible redox couples and one irreversible redox peak at room temperature.

The reversible redox couple was identified as E3, where the $E3_{1/2}$ was observed at 0.61 V (DEP_1 = 255 mV, I_{pc}/I_{pa} = 1). The $E_{1/2}$ values of the quasi-reversible processes E1, E2 and E4 were observed at -0.625 V (DEP_1 = 130 mV), -0.05 V (DEP_1 = 500 mV) and 1.17 V (DEP_1 = 90 mV), respectively. Furthermore, the potential of the irreversible reduction peak identified as E5 was 1.62 V. Theoretically, a DEP of more than 90 mV indicates that more than one electron was involved for each redox reaction. However, in comparison with the ferrocene internal standard with an $E_{1/2}$ at 0.623 V and $DEP_{Fc/Fc+}$ = 450 mV, the observed reversible and quasi-reversible processes were one-electron redox processes.

The redox couples of E1, E2 and E3 were attributed to the formal reduction of Ru(III)/(II) and oxidation of W(IV)/(V) and W(V)/(VI), respectively, whereas E4 and E5 were most likely due to the formal reduction and oxidation of the ligands, respectively. Overall, the redox processes of the metal centres in the BM could be described by the following redox potentials:

$$\text{Ru(II)W(IV)} \rightleftharpoons \left[\text{Ru(III)W(IV)}\right]^{-e} \rightleftharpoons \left[\text{Ru(III)W(V)}\right]^{-2e} \rightleftharpoons \left[\text{Ru(II)W(VI)}\right]^{-2e}$$

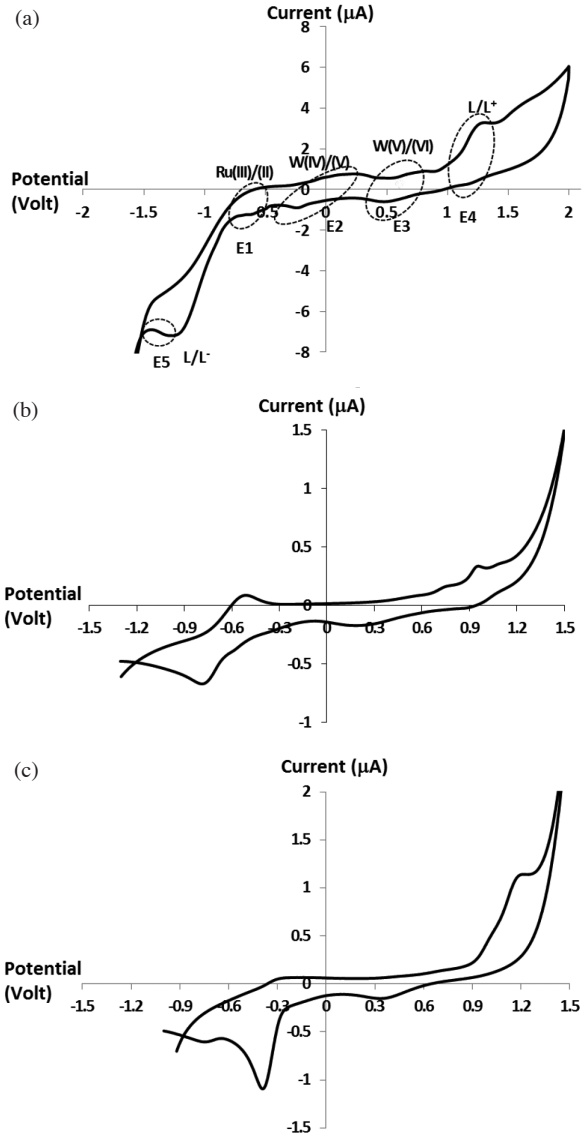

FIGURE 1. The cyclic voltammogram of (a) BM, compared to the monometallic components (b) [$Ru(dmtbpy)_2NCS_2$] and (c) [$W(S_2C_2Ph_2)_2(CO)_2$] in DMF/(1×10^{-4} M) with $TBAPF_6$ supporting electrolyte. Ag/AgCl was used as the reference and the scan rate was 0.1 Vs^{-1}

The electrochemical properties of BM consisted of the constituents monometallic complex properties. The results were similar to the properties of the [(bipy)Ru(m-bpm)PdMe(NCMe)]$(BF_4)_3$ bimetallic complex reported previously (Argazzi et al. 2001; Inagaki & Akita 2010).

The current density of the electrode under various incident photoenergies was evaluated in a PEC cell (Mark-Lee et al. 2013). Photocurrent values were obtained from the difference in currents measured in the dark and under irradiation. This measurement was performed at various potentials and the current changes during irradiation were monitored and recorded. For the purpose of comparison, the photocurrent of BM and N_3 commercial dyes sensitizer were recorded with the same parameters. Current density

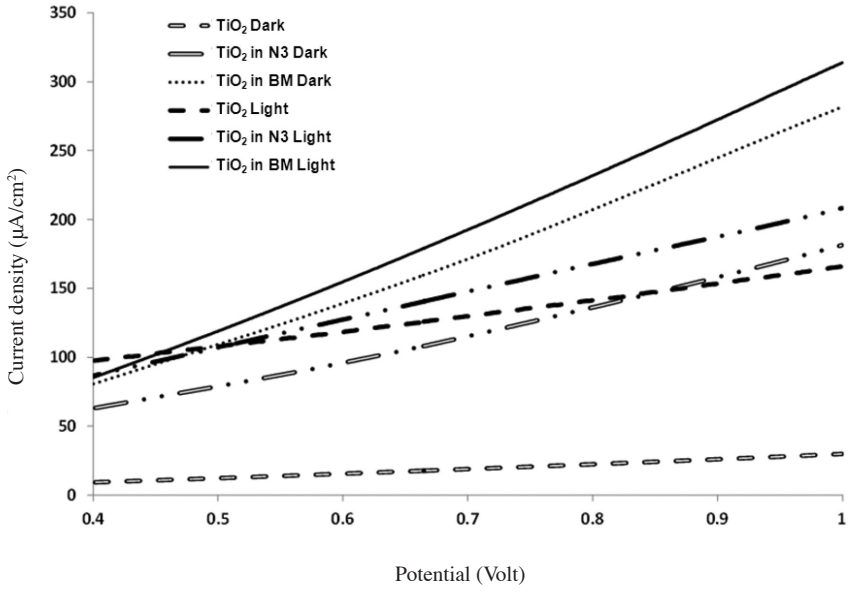

FIGURE 2. The light and dark current density of the TiO_2 photoelectrode in solvent containing the photosensitizer molecule

measurement was performed in homogenous system and under an N_2 atmosphere systems. The photosensitizer was dissolved in triple-distilled water/DMF (4:1) mixture (Katakis et al. 1992) and a TiO_2 thin film was used as the working electrode.

The current density produced under illumination and in the dark for TiO_2 electrode in solution with and without the photosensitizer is shown in Figure 2. The current density of the TiO_2 electrode in solution without the photosensitizer was lower than the solution containing the photosensitizer solution in both under illumination and in the dark. The current density produced by the TiO_2 electrode with BM solution was higher than that of N_3 solution. This result indicated that the BM gave a greater electron density than the N_3 dyes to the TiO_2 electrode, which can inhibit hole- and electron-photogenerated recombination in the UV-excited TiO_2 thin film and increase the photocurrent production. The photocurrent was attributed to the generation of electron–hole pairs in the surface layer of the irradiated TiO_2 electrode and could speed up the reduction of H^+ to H_2 in water-splitting reaction.

CONCLUSION

A thiocyanate bridged bimetallic complex of ruthenium and tungsten BM, consisted of ruthenium bipyridyl and tungsten dithiolene bridged moieties was successfully synthesized. The photophysical, electrochemical and PEC data showed that BM could be used as a dye sensitizer in an artificial photosynthesis system. The sensitizing performance was slightly better that the commercial N_3 dye in homogenous system with TiO_2 photocatalyst. Therefore, further improvement on the BM molecule by introducing an anchoring group (e.g. COOH) to facilitate chemical bonding to photoelectrode can be carried in order to increase the efficiency of the charge transfer process.

ACKNOWLEDGEMENTS

The authors would like to thank Universiti Kebangsaan Malaysia for sponsoring this project under the UKM-GUP-07-30-190, UKM-AP-TK-08-2010 and UKM-OUP-TK-16/73 Research Grants.

REFERENCES

Abe, R., Hara, K., Sayama, K., Domen, K. & Arakawa, H. 2000. Steady hydrogen evolution from water on eosin Y-fixed TiO_2 photocatalyst using a silane-coupling reagent under visible light irradiation. *Journal of Photochemistry and Photobiology A: Chemistry* 137: 63-69.

Aiga, F. & Tada, T. 2005. Design of novel efficient sensitizing dye for nanocrystalline TiO_2 solar cell; tripyridinethiolato (4,4';4"-tricarboxy-2,2':6';2"-terpyridine)ruthenium(II). *Solar Energy Materials and Solar Cells* 85: 437-446.

Allakhverdiev, S.I., Thavasi, V., Kreslavski, V.D., Zharmukhamedov, S.K., Klimov, V.V., Ramakrishna, S., Los, D.A., Mimurod, M., Nishihara, H. & Carpentier, R. 2010. Photosynthetic hydrogen production. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 11: 101-113.

Argazzi, R., Bertolasi, E., Chiorboli, C., Bignozzi, C.A., Itokazu, M.K. & Murakami Iha, N.Y. 2001. Intramolecular energy transfer processes in binuclear Re-Os complexes. *Inorganic Chemistry* 40(27): 6885-6891.

Arifin, K., Daud, W.R.W. & Kassim, M.B. 2011. A novel heterobinuclear complex based on ruthenium-tungsten metals in artificial photosynthesis technology. *The 3rd International Conference on Fuel Cell & Hydrogen Technology (ICFCHT 2011)*. Kuala Lumpur, Malaysia.

Arifin, K., Majlan, E.H., Daud, W.R.W. & Kassim, M.B. 2012. Bimetallic complexes in artificial photosynthesis for hydrogen production: A review. *International Journal of Hydrogen Energy* 37: 3066-3087.

Arifin, K., Daud, W.R.W. & Kassim, M.B. 2012. Optical and photoelectrochemical properties of a TiO_2 thin film doped with a ruthenium–tungsten bimetallic complex. *Ceramic International* 39(3): 2699-2707.

Asali, K.J. & Janaydeh, H.A. 2003. Synthesis and ligand-substitution reactions of $[Et_4N][M(CO)_5SCPh_3]$ (M = W, Mo). *Acta Chimica Slovaca* 50: 677-686.

Balzani, V. & Juris, A. 2001. Photochemistry and photophysics of Ru(II)---polypyridine complexes in the Bologna group. From early studies to recent developments. *Coordination Chemistry Reviews* 211(1): 97-115.

Balzani, V., Juris, A., Venturi, M., Campagna, S. & Serroni, S. 1996. Luminescent and redox-active polynuclear transition metal complexes. *Chemistry Reviews* 96(2): 759-834.

Banerjee, S., Wu, B., Lassahn, P-G., Janiak, C. & Ghosh, A. 2005. Synthesis, structure and bonding of cadmium(II) thiocyanate systems featuring nitrogen based ligands of different denticity. *Inorganica Chimica Acta* 358: 535-544.

Chakraborty, S., Munshi, P. & Lahiri, G.K. 1999. Dinuclear ruthenium(II) bipyridine complexes having non-symmetric α,α'-diimine based neutral bridging ligands. Synthesis, spectroscopic and electrochemical properties. *Polyhedron* 18: 1437-1444.

Chandrasekaran, P., Arumugam, K., Jayarathne, U., Perez, L.M., Mague, J.T. & Donahue, J.P. 2009. Synthesis, structures, and properties of mixed dithiolene-carbonyl and dithiolene-phosphine complexes of tungsten. *Inorganic Chemistry* 48(5): 2103-2113.

Chiorboli, C., Bignozzi, C.A., Scandola, F., Ishow, E.N., Gourdon, A. & Launay, J-P. 1999. Photophysics of dinuclear Ru(II) and Os(II) complexes based on the tetrapyrido[3,2-a:2′,3′-c:3″,2″-h:2‴-3‴-j]phenazine (tpphz) bridging ligand. *Inorganic Chemistry* 38(10): 2402-2410.

Coates, J. 2000. Interpretation of infrared spectra, a practical approach. In *Encyclopedia of Analytical Chemistry*, edited by Meyers, R.A. Chichester: John Wiley & Sons Ltd. pp. 1-24.

Goddard, C.A. & Holm, R.H. 1999. Synthesis and reactivity aspects of the bis(dithiolene) chalcogenide series $[WIVQ(S_2C_2R_2)_2]_2$-(Q = O, S, Se). *Inorganic Chemistry* 38: 5389-5398.

Grätzel, M. 2003. Dye-sensitized solar cells. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 4: 145-153.

Hofmeiera, H. & Schubert, U.S. 2004. Recent developments in the supramolecular chemistry of terpyridine–metal complexes. *Chemical Society Reviews* 33: 373-399.

Inagaki, A. & Akita, M. 2010. Visible-light promoted bimetallic catalysis. *Coord. Chem. Rev.* 254: 1220-1239.

Joya, K.S. & de Groot, H.J.M. 2012. Biomimetic molecular water splitting catalysts for hydrogen generation. *International Journal of Hydrogen Energy* 37(10): 8787-8799.

Katakis, D., Mitsopoulou, C. & Konstantatos, J. 1992. Photocatalytic splitting of water. *Journal of Photochemistry and Photobiology A: Chemistry* 68: 375-388.

Klein, C., Nazeeruddin, M.K., Liska, P., Censo, D.D., Hirata, N., Palomares, E., Durrant, J.R. & Grätzel, M. 2005. Engineering of a novel ruthenium sensitizer and its application in dye-sensitized solar cells for conversion of sunlight into electricity. *Inorganic Chemistry* 44(2): 178-180.

Kleverlaan, C.J., Indelli, M.T., Bignozzi, C.A., Pavanin, L., Scandola, F., Hasselman, G.M. & Meyer, G.J. 2000. Stepwise charge separation in heterotriads. binuclear Ru(II)-Rh(III) complexes on nanocrystalline titanium dioxide. *Journal of American Chemical Society* 122(12): 2840-2849.

Mark-Lee, W.F., Ng, K-H, Minggu, L.J. Umar, A.A. & Kassim, M.B. 2013. A molybdenum dithiolene complex as a potential photosensitiser for photoelectrochemical cells. *International Journal of Hydrogen Energy* 38(22): 9578-9584.

Minggu, L.J., Wan Daud, W.R. & Kassim, M.B. 2010. An overview of photocells and photoreactors for photoelectrochemical water splitting. *International Journal of Hydrogen Energy* 35(11): 5233-5244.

Najafpour, M.M. & Allakhverdiev, S.I. 2012. Manganese compounds as water oxidizing catalysts for hydrogen production via water splitting: From manganese complexes to nano-sized manganese oxides. *International Journal of Hydrogen Energy* 37(10): 8753-8764.

Navarro, J.A.R., Romero, M.A., Salas, J.M., Quiros, M. & Tiekink, E.R.T. 1997. First example of equatorial disposition of end-to-end thiocyanate bridges in a polynuclear copper(II) complex and its relation to the very efficient transmission of the magnetic interaction. *Inorganic Chemistry* 36(22): 4988-4991.

Nazeeruddin, M.K., Klein, C., Liska, P. & Gratzel, M. 2005. Synthesis of novel ruthenium sensitizers and their application in dye-sensitized solar cells. *Coordination Chemistry Reviews* 249: 1460-1467.

Pathania, M.S., Sheikh, H.N. & Kalsotra, B.l. 2007. Synthesis and characterization of tungsten carbonyl complexes containing N-methyl substituted urea and thiourea ligands. *Journal of Coordination Chemistry* 60(13): 1395-1402.

Schrauzer, G.N., Mayweg, V.P. & Heinrich, W. 1965. Concerning the synthesis of dithio-α-diketone complexes of transition metals from thiophospahates of 1,2-dithiols,. *Inorganic Chemistry* 4: 1615-1617.

Shen, L. & Feng, X. 2002. Synthesis and crystal structure of a novel polymericThiocyanato-bridged heteronuclear complex of copper(II) and cadmium(II). *Structural Chemistry* 13: 437-441.

Vougioukalakis, G.C., Philippopoulos, A.I., Stergiopoulos, T. & Falaras, P. 2011. Contributions to the development of ruthenium-based sensitizers for dye-sensitized solar cells. *Coordination Chemistry Reviews* 255: 2602-2621.

Ward, M.D. & McCleverty, J.A. 2002. Non-innocent behaviour in mononuclear and polynuclear complexes: Consequences for redox and electronic spectroscopic properties. *Journal of Chemical Society Dalton Transactions* 3: 275-288.

Young, K.J., Martini, L.A., Milot, R.L., Snoeberger Iii, R.C., Batista, V.S., Schmuttenmaer, C.A., Crabtree, R.H. & Brudvig, G.W. 2012. Light-driven water oxidation for solar fuels. *Coordination Chemistry Reviews* 256(21-22): 2503-2520.

Zhao, S., Liu, X., Feng, W., Lu, X., Wong, W-Y. & Wong, W-K. 2012. Effective enhancement of near-infrared emission by carbazole modification in the Zn-Nd bimetallic Schiff-base complexes. *Inorganic Chemistry Communications* 20: 41-45.

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Received: 22 November 2012
Accepted: 9 April 2013